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# Optimized effective potential method: Is it possible to obtain an accurate representation of the response function for finite orbital basis sets?

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The optimized effective potential (OEP) equations are solved in a matrix representation using the orbital products of occupied and virtual orbitals for the representation of both the local potential and the response function. This results in a direct relationship between the matrix elements of local and nonlocal operators for the exchange-correlation potential. The effect of the truncation of the number of such products in the case of finite orbital basis sets on the OEP orbital and total energies and on the spectrum of eigenvalues of the response function is examined. Test calculations for Ar and Ne show that rather large AO basis sets are needed to obtain an accurate representation of the response function. © 2007 American Institute of Physics. [DOI: 10.1063/1.2777144]

## I. INTRODUCTION

In conventional Kohn-Sham density functional theory (KS-DFT),<sup>1</sup> the exchange-correlation energy is represented by an explicit functional of the density in both the local density approximation<sup>2</sup> and the generalized gradient approximation.<sup>3</sup> However, one may also consider orbital-dependent functionals which are implicit functionals of the electron density because the Kohn-Sham orbitals are uniquely determined by the electron density as a consequence of the Hohenberg-Kohn theorem.<sup>4</sup> This is the subject of the optimized effective potential (OEP) method.<sup>5,6</sup> Note that the kinetic energy of the noninteracting system in conventional KS-DFT methods is already represented by an orbital-dependent functional. The most evident orbital-dependent functional is of course given by the Hartree-Fock (HF) energy expression, which contains the exchange energy in orbital-dependent form. The variational optimization of the HF energy functional under the additional constraint of a local exchange potential is denoted as optimized effective potential exchange-only (OEPx) method.<sup>5,6</sup> The local exchange potential is obtained by solving an integral equation which has first been given by Sharp and Horton<sup>5</sup> and solved for atoms by Talman and Shadwick.<sup>6</sup> Since then the OEP method has been discussed extensively.<sup>7–26</sup> Approximations to OEPx such as the method of Krieger-Li-Iafrate (KLI),<sup>25,26</sup> the local Hartree-Fock method,<sup>27</sup> and the effective local potential<sup>28</sup> have also been reported.

The subject of this Contribution is the formulation of the OEP problem in matrix form using the products of occupied and virtual orbitals as an expansion basis for both the response function and the local potential. It is important to note that, because the solutions of the OEP problem rely on the response function, they can be expected to be much more sensitive to the choice of the orbital basis set than the HF solution. In the latter case, it is sufficient to choose a basis set appropriate for a representation of only the occupied or-

bitals with no particular role for the virtual orbitals. In the case of OEP, however, one has to deal with the response function which involves an infinite sum over virtual orbitals. As far as we know, the effects of the truncation of this sum for finite orbital basis sets have not yet been studied systematically. The present Contribution is intended as a first step to fill this gap.

A matrix representation of the OEP integral equation will be developed in Sec. II. In Sec. III, the resulting formalism will be used to study the influence of the AO basis set on the solution of the OEP equations for the noble gas atoms neon and argon in the case of the exchange-only approximation.

## II. THE OEP EQUATIONS IN A MATRIX REPRESENTATION

In the OEP method, one seeks for a local potential  $V_\sigma(\mathbf{r})$  such that the eigenfunctions  $\psi_{p\sigma}$  of the one-electron Schrödinger equation,

$$\hat{F}_\sigma \psi_{p\sigma}(\mathbf{r}) = \epsilon_{p\sigma} \psi_{p\sigma}(\mathbf{r}), \quad (1)$$

with the KS Hamiltonian,

$$\hat{F}_\sigma = -\frac{1}{2}\Delta + V_\sigma(\mathbf{r}) \quad (2)$$

minimize the total energy given by

$$\begin{aligned} E^{\text{OEP}}[\{\psi_{i\sigma}\}] = & \sum_\sigma \sum_i \int \psi_{i\sigma}^*(\mathbf{r}) \left( -\frac{1}{2}\Delta \right) \psi_{i\sigma}(\mathbf{r}) d^3\mathbf{r} \\ & + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3\mathbf{r} \\ & + \frac{1}{2} \int \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \\ & + E_{\text{xc}}[\{\psi_{i\sigma}\}]. \end{aligned} \quad (3)$$

$\rho(\mathbf{r}) = \sum_\sigma \sum_i |\psi_{i\sigma}(\mathbf{r})|^2$  is the electron density and  $E_{\text{xc}}[\{\psi_{i\sigma}\}]$  is the orbital-dependent exchange-correlation energy.  $\sigma$  labels the two possible spin orientations  $\alpha$  (spin up) and  $\beta$  (spin

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down). We use labels  $i, j, \dots$  for occupied orbitals,  $a, b, \dots$  for unoccupied orbitals, and  $p, q, \dots$  for general orbitals. The orbital-dependent exchange energy adopted from HF theory is given by

$$E_x[\{\psi_{i\sigma}\}] = -\frac{1}{2} \sum_{\sigma} \sum_{i,j} \int \frac{\psi_{i\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \psi_{j\sigma}^*(\mathbf{r}') \psi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (4)$$

Conventionally,  $V_{\sigma}(\mathbf{r})$  is written as

$$V_{\sigma}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + V_{\sigma}^{\text{xc}}(\mathbf{r}), \quad (5)$$

where  $V_{\text{ext}}$  is the external potential which is, in general, given by the Coulomb potential of the nuclei.  $V_{\sigma}^{\text{xc}}(\mathbf{r})$  is the local exchange-correlation potential arising from minimization of the energy [Eq. (3)]. It can be found from the integral equation<sup>5</sup>

$$\sum_i \sum_a \left( \frac{\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r})}{\epsilon_{a\sigma} - \epsilon_{i\sigma}} (v_{ia,\sigma}^{\text{xc}} - v_{ia,\sigma}^{\text{xc, nl}}) + \frac{\psi_{i\sigma}^*(\mathbf{r}) \psi_{a\sigma}(\mathbf{r})}{\epsilon_{a\sigma} - \epsilon_{i\sigma}} (v_{ai,\sigma}^{\text{xc}} - v_{ai,\sigma}^{\text{xc, nl}}) \right) = 0, \quad (6)$$

with

$$v_{ia,\sigma}^{\text{xc}} = \int \psi_{i\sigma}^*(\mathbf{r}) V_{\sigma}^{\text{xc}}(\mathbf{r}) \psi_{a\sigma}(\mathbf{r}) d^3\mathbf{r} \quad (7)$$

and

$$v_{ia,\sigma}^{\text{xc, nl}} = \int \frac{\delta E_{\text{xc}}[\{\psi_{j\sigma}\}]}{\delta \psi_{i\sigma}(\mathbf{r})} \psi_{a\sigma}(\mathbf{r}) d^3\mathbf{r}. \quad (8)$$

Defining the response function as

$$\chi_{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_i \sum_a \frac{1}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} (\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \psi_{i\sigma}^*(\mathbf{r}') \psi_{a\sigma}(\mathbf{r}') + \psi_{a\sigma}(\mathbf{r}) \psi_{i\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}') \psi_{a\sigma}^*(\mathbf{r}')), \quad (9)$$

Eq. (6) can be rewritten as

$$\int \chi_{\sigma}(\mathbf{r}, \mathbf{r}') V_{\sigma}^{\text{xc}}(\mathbf{r}') d^3\mathbf{r}' + \sum_i \sum_a \left( \frac{\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r})}{\epsilon_{a\sigma} - \epsilon_{i\sigma}} v_{ia,\sigma}^{\text{xc, nl}} + \frac{\psi_{i\sigma}^*(\mathbf{r}) \psi_{a\sigma}(\mathbf{r})}{\epsilon_{a\sigma} - \epsilon_{i\sigma}} v_{ai,\sigma}^{\text{xc, nl}} \right) = 0. \quad (10)$$

If the products  $\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r})$  comprised a linearly independent set of functions, the only possible solution of Eq. (6) would be  $v_{ia,\sigma}^{\text{xc}} = v_{ia,\sigma}^{\text{xc, nl}}$ . In this particular case, the restriction to a local potential  $V_{\sigma}(\mathbf{r})$  would not make any difference with respect to the energy and density matrix resulting from the variational optimization of the energy [Eq. (3)]. For a complete basis, however, the product set is linearly dependent except for two-electron closed-shell systems such as  $\text{H}_2$  or He. Although it still seems as if  $v_{ia,\sigma}^{\text{xc}} = v_{ia,\sigma}^{\text{xc, nl}}$  represents a trivial solution of Eq. (6) even for a linearly dependent product basis, it has been shown that this is not the case.<sup>11</sup> It is therefore of interest to find a relationship between the matrix

elements  $v_{ia,\sigma}^{\text{xc}}$  and  $v_{ia,\sigma}^{\text{xc, nl}}$  of local and nonlocal operators in the general case of a linearly dependent set of orbital products  $\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r})$ .

From hereon we will drop the spin label  $\sigma$  because the structure of the OEP equations is the same for both spin orientations. We will also restrict ourselves to real orbital basis sets. Introducing the abbreviations,

$$\begin{aligned} \Psi_{ia}(\mathbf{r}) &\equiv \frac{\psi_a(\mathbf{r}) \psi_i(\mathbf{r})}{\sqrt{\epsilon_a - \epsilon_i}}, \\ z_{ia} &\equiv \frac{v_{ia}^{\text{xc}}}{\sqrt{\epsilon_a - \epsilon_i}}, \\ z_{ia}^{\text{nl}} &\equiv \frac{v_{ia}^{\text{xc, nl}}}{\sqrt{\epsilon_a - \epsilon_i}}, \end{aligned} \quad (11)$$

Eq. (6) can be rewritten as

$$\sum_{ia} \Psi_{ia}(\mathbf{r}) (z_{ia} - z_{ia}^{\text{nl}}) = 0. \quad (12)$$

Before casting Eq. (12) into the form of a matrix equation, a general definition of the scalar product has to be given. We have<sup>29</sup>

$$(f|g) \equiv \int d^3\mathbf{r} d^3\mathbf{r}' f(\mathbf{r}) \mathcal{W}(\mathbf{r} - \mathbf{r}') g(\mathbf{r}'). \quad (13)$$

Equation (13) fulfills all the conditions for a scalar product if the Fourier transform of the integral kernel  $\mathcal{W}(\mathbf{r} - \mathbf{r}')$  is positive definite.<sup>29</sup> In practice, only two choices are of interest:  $\mathcal{W}(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$  and  $\mathcal{W}(\mathbf{r} - \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ , leading to overlap and Coulomb integrals, respectively. Using Eq. (13) to define the metric of the vector space spanned by the set  $\{\Psi_{ai}\}$  as

$$M_{jb,ia} \equiv (\Psi_{jb} | \Psi_{ia}), \quad (14)$$

we obtain from Eq. (12) by forming the scalar product with  $\Psi_{jb}$ ,

$$\sum_{ia} M_{jb,ia} (z_{ia} - z_{ia}^{\text{nl}}) = 0. \quad (15)$$

An important step in the solution of the OEP equation is the choice of an appropriate basis for the expansion of the local exchange-correlation potential. This potential is not a square integrable function because it falls off as  $-1/r$  asymptotically. It is therefore not possible to expand it directly in a square integrable basis using the integral kernel  $\mathcal{W}(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$  for the formation of the scalar product. Instead, one has to expand the charge density generating the local potential corresponding to  $\mathcal{W}(\mathbf{r} - \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ . Using the abbreviation Eq. (11) in Eq. (9) and assuming real orbitals, the response function can be written as

$$\chi(\mathbf{r}, \mathbf{r}') = -2 \sum_{ia} \Psi_{ia}(\mathbf{r}) \Psi_{ia}(\mathbf{r}'). \quad (16)$$

It can be seen from Eq. (16) that the response function projects onto the space spanned by the product basis  $\Psi_{ia}(\mathbf{r})$ . Thus, it is a natural choice to employ the same basis in the expansion of the local potential. It has been shown that, pro-

vided that the orbital basis is complete, the product basis  $\Psi_{ia}(\mathbf{r})$  spans the complete space with the only exception of a single function representing a constant.<sup>14</sup> The asymptotic decay of the exchange-correlation potential as  $-1/r$  requires the charge density generating this potential to integrate to  $-1$ . Since the functions  $\Psi_{ia}(\mathbf{r})$  integrate to zero, thus being unable to produce a net charge, it is necessary to add one additional function  $g(\mathbf{r})$  to the expansion basis. This function is normalized such that

$$\int g(\mathbf{r}) d^3\mathbf{r} = 1. \quad (17)$$

Denoting the expansion coefficients as  $\tilde{w}_{ia}$ , one obtains

$$V^{\text{xc}}(\mathbf{r}) = V_0^{\text{xc}}(\mathbf{r}) + \Delta V^{\text{xc}}(\mathbf{r}), \quad (18)$$

with

$$V_0^{\text{xc}}(\mathbf{r}) = \sum_{ia} \int \frac{\Psi_{ia}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' \tilde{w}_{ia} \quad (19)$$

and

$$\Delta V^{\text{xc}}(\mathbf{r}) = - \int \frac{g(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}'. \quad (20)$$

The expansion coefficient of  $g(\mathbf{r})$  is restricted to  $-1$  by the asymptotic condition. Thus, only the contribution  $V_0^{\text{xc}}(\mathbf{r})$  to the exchange-correlation potential has to be determined. The function  $g(\mathbf{r})$  still needs to be specified. A very common choice is

$$g(\mathbf{r}) = \frac{1}{N} \rho(\mathbf{r}), \quad (21)$$

where  $N = N_\alpha + N_\beta$  represents the total number of electrons. Inserting Eq. (21) into Eq. (20) and adding this contribution to the second term on the right-hand side of Eq. (5) lead to the Fermi-Amaldi potential. Another possible choice is the charge density resulting from the highest occupied molecular orbital (HOMO),

$$g(\mathbf{r}) = |\psi_{\text{HOMO}}(\mathbf{r})|^2. \quad (22)$$

The energy-weighted matrix elements of the two components of the potential are defined as

$$w_{ia} \equiv \int \Psi_{ia}(\mathbf{r}) V_0^{\text{xc}}(\mathbf{r}) d^3\mathbf{r} \quad (23)$$

and

$$\Delta w_{ia} \equiv \int \Psi_{ia}(\mathbf{r}) \Delta V^{\text{xc}}(\mathbf{r}) d^3\mathbf{r}. \quad (24)$$

From Eqs. (7), (11), (18), (23), and (24), one obtains

$$z_{ia} = w_{ia} + \Delta w_{ia}. \quad (25)$$

Inserting Eq. (25) into Eq. (15) and absorbing the matrix elements of  $\Delta w_{ia}$  into the nonlocal part by writing

$$w_{ia}^{\text{nl}} = z_{ia}^{\text{nl}} - \Delta w_{ia} \quad (26)$$

lead to

$$\sum_{ia} M_{jb,ia} (w_{ia} - w_{ia}^{\text{nl}}) = 0 \quad (27)$$

or, in matrix form,

$$\mathbf{M}(\mathbf{w} - \mathbf{w}^{\text{nl}}) = 0. \quad (28)$$

Using Eq. (19) in Eq. (23) and taking into account the definition Eq. (14) of the metric, the relationship between the matrix elements  $w_{ia}$  and the expansion coefficients  $\tilde{w}_{ia}$  is obtained as

$$w_{ia} = \sum_{jb} M_{ia,jb} \tilde{w}_{jb} \quad (29)$$

or, in matrix form,

$$\mathbf{w} = \mathbf{M} \tilde{\mathbf{w}}. \quad (30)$$

Inserting Eq. (30) into Eq. (28) gives

$$\mathbf{M}^2 \tilde{\mathbf{w}} = \mathbf{M} \mathbf{w}^{\text{nl}}. \quad (31)$$

Equation (31) is the matrix form of the OEP equation [Eq. (6)], with  $\mathbf{M}^2$  corresponding to the matrix representation of the response function [Eq. (16)].

It is important to note that Eq. (31) provides a solution for the coefficients  $\tilde{w}_{ia}$  even in the case of a singular matrix  $\mathbf{M}$ . The equation

$$\mathbf{M} \tilde{\mathbf{w}} = \mathbf{w}^{\text{nl}}, \quad (32)$$

on the other hand, can, in general, only be solved if the matrix  $\mathbf{M}$  is invertible which corresponds to the case of a linearly independent product basis  $\Psi_{ia}(\mathbf{r})$ . Equations (31) and (32) would then be equivalent.

Interestingly, the form of Eq. (32) is invariant with respect to a renormalization of the basis vectors  $\Psi_{ia}$ . Arranging these in a row vector  $\Psi$ , one may write

$$\Psi = \Psi' \mathbf{d}. \quad (33)$$

$\mathbf{d}$  is a diagonal matrix containing positive numbers, thus only changing the norm of the vectors. Replacing the expansion basis  $\Psi_{ia}$  of the local potential in Eq. (19) with the primed basis  $\Psi'_{ia}$ , the corresponding (primed) expansion coefficients are given by

$$\tilde{\mathbf{w}}' = \mathbf{d} \tilde{\mathbf{w}}. \quad (34)$$

The metric of the primed basis consisting of the matrix elements  $M'_{ia,jb} = (\Psi'_{ia} | \Psi'_{jb})$  is related to that of the unprimed basis by

$$\mathbf{M} = \mathbf{d} \mathbf{M}' \mathbf{d}. \quad (35)$$

Finally, renormalization of the vector components on the right-hand side of Eq. (32) yields

$$\mathbf{w}^{\text{nl}} = \mathbf{d} \mathbf{w}^{\text{nl}'}. \quad (36)$$

Using Eqs. (34)–(36), Eq. (32) can be rewritten as

$$\mathbf{M}' \tilde{\mathbf{w}}' = \mathbf{w}^{\text{nl}'}. \quad (37)$$

Note that, in contrast to Eq. (32), Eq. (31) is not invariant against replacement of the unprimed by the primed matrix elements. Choosing  $d_{ia,ia} = (\epsilon_a - \epsilon_i)^{-1/2}$ , it can be seen from Eq. (11) that the primed basis is just given by orbital prod-

ucts  $\psi_i\psi_a$  without any energy denominators. Equation (37) is then equivalent to Eq. (12) in the paper of Staroverov *et al.*,<sup>24</sup> provided that the Coulomb integral kernel  $\mathcal{W}(\mathbf{r}-\mathbf{r}')=|\mathbf{r}-\mathbf{r}'|^{-1}$  is employed for the formation of the scalar product. We would like to emphasize that this equation can only be solved if the metric formed by the elements  $(\psi_i\psi_a|\psi_j\psi_b)$  is strictly invertible, which is only the case for sufficiently small basis sets. In the next section, we will present evidence that such basis sets might be too small for an appropriate solution of the OEP equations.

The energy denominators can be eliminated from Eq. (32) by an appropriate choice of the renormalization matrix  $\mathbf{d}$ , leading to Eq. (37) but not from Eq. (31). Replacement of the energy denominators in Eq. (31) by a constant leads to the so-called common energy denominator approximation (CEDA) developed by Gritsenko and Baerends<sup>16</sup> and advocated by Izmaylov *et al.*<sup>30</sup> and does no longer correspond to an exact solution of the OEP equations.

In general, the basis  $\Psi_{ia}(\mathbf{r})$  is neither orthonormal nor linearly independent. Thus, the matrix  $\mathbf{M}$  is singular. Equation (31) can then be solved by using an orthonormal basis resulting from the canonical orthogonalization scheme of Löwdin.<sup>31</sup> It is obtained by diagonalizing the metric  $\mathbf{M}$  as

$$\mathbf{U}^\dagger \mathbf{M} \mathbf{U} = \boldsymbol{\lambda}. \quad (38)$$

A real orthonormal basis  $\{f_\mu\}$  is given by

$$f_\mu(\mathbf{r}) = \frac{1}{\sqrt{\lambda_\mu}} \sum_{ia} \Psi_{ia}(\mathbf{r}) U_{ia,\mu} \quad (39)$$

for any index  $\mu$  which corresponds to  $\lambda_\mu \neq 0$ . The remaining eigenfunctions corresponding to  $\lambda_\mu = 0$  form the null space because the corresponding linear combinations  $\sum_{ia} \Psi_{ia}(\mathbf{r}) U_{ia,\mu}$  of the orbital products are zero vectors. The two subspaces will be distinguished by writing  $\mu \in \mathcal{L}$  and  $\mu \in \mathcal{K}$  for indices corresponding to the space of linearly independent functions and to the null space, respectively. Exploiting the unitarity of the transformation matrix  $\mathbf{U}$  in Eq. (39), the orbital products can be expressed in terms of the new basis as

$$\Psi_{ia}(\mathbf{r}) = \sum_{\mu \in \mathcal{L}} \sqrt{\lambda_\mu} f_\mu(\mathbf{r}) U_{\mu,ia}^\dagger. \quad (40)$$

Using Eq. (40), the response function [Eq. (16)] is obtained in the basis  $\{f_\mu\}$  as

$$\chi(\mathbf{r}, \mathbf{r}') = -2 \sum_{\mu \in \mathcal{L}} \lambda_\mu f_\mu(\mathbf{r}) f_\mu(\mathbf{r}'). \quad (41)$$

Thus, the basis functions  $f_\mu(\mathbf{r})$  are eigenfunctions of the response operator with the corresponding eigenvalues being given by  $-2\lambda_\mu$ . The charge density generating the component  $V_0^{\text{xc}}$  of the local exchange-correlation potential can also be expanded in the new basis set  $\{f_\mu\}$ ,

$$V_0^{\text{xc}}(\mathbf{r}) = \sum_{\mu \in \mathcal{L}} \int \frac{f_\mu(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' v_\mu. \quad (42)$$

Inserting Eq. (39) into Eq. (42), the expansion coefficients  $\tilde{w}_{ia}$  are obtained from comparison with Eq. (19) as

$$\tilde{w}_{ia} = \sum_{\mu \in \mathcal{L}} U_{ia,\mu} \frac{v_\mu}{\sqrt{\lambda_\mu}} \quad (43)$$

or

$$\tilde{\mathbf{w}} = (\mathbf{U}\boldsymbol{\lambda}^{-1/2})^\mathcal{L} \mathbf{v}. \quad (44)$$

From hereon the superscript  $\mathcal{L}$  indicates that indices corresponding to the null space are excluded from the summation in the matrix product. Using the unitarity of the matrix  $\mathbf{U}$ , the inverse transformation is given by

$$\mathbf{v} = \boldsymbol{\lambda}^{1/2} \mathbf{U}^\dagger \tilde{\mathbf{w}}. \quad (45)$$

We now return to Eq. (31) which is our starting point for the solution of the OEP problem. Multiplying both sides of Eq. (31) by  $\mathbf{U}^\dagger$  from the left, inserting the unit matrix  $\mathbf{U}\mathbf{U}^\dagger$ , and using Eq. (38), we obtain

$$\boldsymbol{\lambda}^2 \mathbf{U}^\dagger \tilde{\mathbf{w}} = \boldsymbol{\lambda} \mathbf{U}^\dagger \mathbf{w}^{\text{nl}}. \quad (46)$$

It is important to note that both sides of Eq. (46) vanish for  $\mu \in \mathcal{K}$  because  $\lambda_\mu = 0$  in this case. This provides a formal solution of Eq. (31) even in the case of a singular matrix  $\mathbf{M}$ . One can use Eq. (45) in Eq. (46) to obtain

$$\mathbf{v} = (\boldsymbol{\lambda}^{-1/2} \mathbf{U}^\dagger)^\mathcal{L} \mathbf{w}^{\text{nl}}. \quad (47)$$

Equation (47) determines the local exchange-correlation potential because it gives its expansion coefficients in the basis  $\{f_\mu\}$ . The expansion coefficients in terms of the orbital products are obtained by inserting Eq. (47) in Eq. (44),

$$\tilde{\mathbf{w}} = (\mathbf{U}\boldsymbol{\lambda}^{-1} \mathbf{U}^\dagger)^\mathcal{L} \mathbf{w}^{\text{nl}}. \quad (48)$$

Inserting Eq. (48) into Eq. (30) and using Eq. (38) finally give

$$\mathbf{w} = (\mathbf{U}\mathbf{U}^\dagger)^\mathcal{L} \mathbf{w}^{\text{nl}}. \quad (49)$$

Equation (49) is one of the major results of the present work. It provides a general relationship between matrix elements of the local ( $w_{ia}$ ) and nonlocal ( $w_{ia}^{\text{nl}}$ ) exchange-correlation operators. This relationship is carried out by the unitary matrix diagonalizing the metric  $\mathbf{M}$ . Note that  $(\mathbf{U}\mathbf{U}^\dagger)^\mathcal{L}$  is, in general, not the unit matrix, so that the matrix elements  $w_{ia}$  and  $w_{ia}^{\text{nl}}$  are not identical. This would only hold if the product basis  $\Psi_{ia}$  was linearly independent. In this case there would be no null space, and therefore  $\sum_\mu U_{ia,\mu} U_{\mu,jb}^\dagger = \delta_{ia,jb}$  and  $w_{ia} = w_{ia}^{\text{nl}}$  as required in this particular case.

Note that Eq. (49) is closely related to a scheme developed by Harriman<sup>32,33</sup> and Hoch and Harriman<sup>34</sup> for the decomposition of a one-electron operator into local and nonlocal components. To demonstrate this analogy we briefly recapitulate the basic idea of Harriman. Any one electron operator  $\hat{G}$  can be represented by an integral kernel  $G(\mathbf{r}, \mathbf{r}')$  in real space. Using a complete orthonormal orbital basis set  $\{\phi_k\}$ , this integral kernel can be expanded as

$$G(\mathbf{r}, \mathbf{r}') = \sum_{ij} \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}') G_{ij}. \quad (50)$$

Because in general,  $\mathbf{r} \neq \mathbf{r}'$ , all product functions  $\phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}')$  are not only linearly independent but also orthonormal. The corresponding vector space collapses into a space of smaller dimension with many linearly dependent products  $\phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}')$



if  $\mathbf{r}=\mathbf{r}'$ . Thus, the original vector space denoted as  $\mathcal{E}$  can be divided into two orthogonal subspaces:  $\mathcal{E}=\mathcal{L}\oplus\mathcal{K}$ , where  $\mathcal{K}$  is the null space of the collapsed operator. The metric of the collapsed products is given by the matrix elements

$$M_{ij,kl}=\int d^3\mathbf{r}\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r})\phi_l(\mathbf{r}). \quad (51)$$

Denoting the unitary matrix diagonalizing this metric as  $\mathbf{U}$ , one may introduce the following basis for the integral kernel:

$$\alpha_\mu(\mathbf{r},\mathbf{r}')=\sum_{ij}\phi_i(\mathbf{r})\phi_j^*(\mathbf{r}')U_{ij,\mu}. \quad (52)$$

Using Eq. (52) and its inverse, the components of the integral kernel appearing in Eq. (50) can be rewritten as

$$G_{ij}=G_{ij}^{\mathcal{L}}+G_{ij}^{\mathcal{K}}, \quad (53)$$

with

$$G_{ij}^{\mathcal{L}}\equiv\sum_{kl}\sum_{\mu\in\mathcal{L}}U_{ij,\mu}U_{\mu,kl}^\dagger G_{kl},$$

$$G_{ij}^{\mathcal{K}}\equiv\sum_{kl}\sum_{\mu\in\mathcal{K}}U_{ij,\mu}U_{\mu,kl}^\dagger G_{kl}. \quad (54)$$

The summation in Eq. (54) runs over indices  $\mu$  corresponding to nonzero (subspace  $\mathcal{L}$ ) and zero (subspace  $\mathcal{K}$ ) eigenvalues of the metric given in Eq. (51). Equation (54) provides a way to divide any one-electron operator into local (subspace  $\mathcal{L}$ ) and nonlocal (subspace  $\mathcal{K}$ ) components. The analogy between Eqs. (54) and (49) is obvious except for the prefactors  $(\epsilon_a-\epsilon_i)^{-1/2}$  present in the product basis of the latter [see Eq. (11)]. Thus, Eq. (49) represents a way to project out the local components from a nonlocal operator.

A practical problem is the separation of the subspaces  $\mathcal{K}$  and  $\mathcal{L}$  because eigenvalues which are exactly zero will never occur in actual calculations due to numerical errors. One is therefore faced with the problem of finding objective criteria for discriminating zero and nonzero eigenvalues.<sup>34,35</sup>

### III. FINITE BASIS SETS

The method developed in the previous section for the solution of the OEP equations can still be applied in the case of a finite orbital basis by just restricting all the summations with respect to virtual orbitals to those available in the limited basis. Because this approach is based exclusively on a unitary matrix obtained from diagonalization of a Hermitian matrix, such an approach should not be plagued by any problems with numerical stability provided that the cutoff parameter for near-zero eigenvalues of the metric is chosen large enough. Problems may arise from the incompleteness of the basis set formed by the MO products  $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$  in the case of a finite orbital basis. As a consequence, the range of the response operator is narrowed down, i.e., there is now an infinite number of linearly independent functions  $f(\mathbf{r}')$  fulfilling

$$\int \chi(\mathbf{r},\mathbf{r}')f(\mathbf{r}')d^3\mathbf{r}'=0 \quad (55)$$

at any point  $\mathbf{r}$ . Remember that there is only one such function given by a constant in the case of a complete orbital basis set.<sup>14</sup> Considering the first term on the left-hand side of Eq. (10), it can be seen that it remains unchanged if a function  $f(\mathbf{r})$  fulfilling Eq. (55) at any point  $\mathbf{r}$  is added to the potential. Assuming that  $V^{\text{xc}}(\mathbf{r})$  solves the OEP equation,  $V^{\text{xc}}(\mathbf{r})+f(\mathbf{r})$  therefore represents another solution, such that one ends up with an infinite number of such potentials.<sup>24</sup> This ambiguity is a consequence of the fact that there is no one-to-one mapping between a local potential and its matrix representation in a finite basis set. It can be avoided by excluding components outside the range of the response operator from the expansion basis of the potential. This is the case if the same basis sets are chosen for the expansion of the potential (or the charge density generating this potential) and the response function as has been done in the previous section [compare Eqs. (41) and (42)]. Note that all functions  $f(\mathbf{r})$  with  $\sum_{ia}(f|\Psi_{ia})(\Psi_{ia}|f)=0$  drop out in a singular value decomposition. The invariance of the solution of Eq. (10) with respect to addition of functions outside the range of the response operator to the potential does not mean that the OEP solution is also invariant. Note that the eigenfunctions and eigenvalues of the one-electron Schrödinger equation [Eq. (1)] entering the response function are changed by the addition of such functions.

Most of the schemes relying on the response function for the solution of the OEP equation in the case of finite orbital basis sets employ an auxiliary basis for the expansion of the local potential.<sup>10,12,14,15,17,20</sup> Since the response function projects this basis onto the space spanned by the orbital products  $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$ , one might try to use these products directly for the expansion of the potential, as has already been done by Colle and Nesbet.<sup>19</sup> This corresponds to the formalism described in the previous section, which provides an exact solution only for complete orbital basis sets. In an attempt to examine the dependence of the OEP results on the size of the AO basis, we use it here in connection with finite basis sets. The use of the Coulomb norm corresponding to the integral kernel  $\mathcal{W}(\mathbf{r}-\mathbf{r}')=|\mathbf{r}-\mathbf{r}'|^{-1}$  for the formation of the scalar product in Eq. (13) has also the practical advantage that the matrix elements of the metric can be expressed in terms of two-electron repulsion integrals available in any quantum chemistry code. No grid and no numerical integration is needed.

In the following, the exchange-only OEP (OEP<sub>x</sub>) method will be considered with the orbital-dependent exchange functional given by Eq. (4). The matrix elements of the nonlocal exchange operator needed for the solution of the OEP problem are then given by

$$v_{ia,\sigma}^{\text{x,nl}}=-\int \psi_{i\sigma}^*(\mathbf{r})\sum_j\frac{\psi_{j\sigma}(\mathbf{r})\psi_{j\sigma}^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_{a\sigma}(\mathbf{r}')d^3\mathbf{r}d^3\mathbf{r}'. \quad (56)$$

For the generation of the correction potential  $\Delta V^{\text{xc}}(\mathbf{r})$  defined in Eq. (20), the alternatives given by Eqs. (21) and (22) have both been employed, but the differences in the numerical

TABLE I. OEPx results for Ne using uncontracted Schmidt-Ruedenberg basis sets of various sizes and the aug-cc-pV6Z basis sets both contracted (*av6z*) and uncontracted (*av6zu*). The first column shows the number of primitive Gaussian-type functions for the *s* and *p* atomic orbitals in the case of the Schmidt-Ruedenberg basis. The threshold for zero eigenvalues of the metric is given in the second column.  $N_v$  is the number of eigenfunctions with nonzero eigenvalues.  $N_p$  is the number of orbital products.  $E^{\text{OEPx}}$  and  $E_x^{\text{OEPx}}$  are the total electronic and the exchange energies, respectively, as obtained from the OEPx calculations. The corresponding HF values are denoted as  $E^{\text{HF}}$  and  $E_x^{\text{HF}}$ . All energies are given in atomic units.

Basis	$\lambda_{\min}$	$N_v$	$N_p$	$E^{\text{OEPx}^a}$	$E_x^{\text{OEPx}^a}$	$E^{\text{HF}}$	$E_x^{\text{HF}}$
<i>av6z</i>	$10^{-5}$	9	18	-128.546 597	-12.107 568	-128.547 062	-12.108 345
<i>av6z</i>	$10^{-6}$	10	18	-128.546 984	-12.108 239		
<i>av6zu</i>	$10^{-5}$	14	40	-128.545 477	-12.105 200	-128.547 062	-12.108 341
<i>av6zu</i>	$10^{-6}$	15	40	-128.545 477	-12.105 200		
16s/8p	$10^{-5}$	12	35	-128.544 924	-12.106 191	-128.546 302	-12.108 847
16s/8p	$10^{-6}$	15	35	-128.544 934	-12.106 203		
18s/9p	$10^{-5}$	13	40	-128.545 289	-12.105 481	-128.546 816	-12.108 583
18s/9p	$10^{-6}$	14	40	-128.545 290	-12.105 483		
20s/10p	$10^{-5}$	13	45	-128.545 331	-12.105 190	-128.546 988	-12.108 464
20s/10p	$10^{-6}$	15	45	-128.545 333	-12.105 197		
22s/11p	$10^{-5}$	14	50	-128.545 445	-12.105 225	-128.547 053	-12.108 408
22s/11p	$10^{-6}$	16	50	-128.545 446	-12.105 226		
24s/12p	$10^{-5}$	14	55	-128.545 426	-12.105 088	-128.547 078	-12.108 381
24s/12p	$10^{-6}$	17	55	-128.545 426	-12.105 088		
26s/13p	$10^{-5}$	15	60	-128.545 410	-12.105 034	-128.547 089	-12.108 366
26s/13p	$10^{-6}$	17	60	-128.545 411	-12.105 035		
28s/14p	$10^{-4}$	11	65	-128.545 415	-12.105 036	-128.547 094	-12.108 359
28s/14p	$10^{-5}$	15	65	-128.545 426	-12.105 055		
28s/14p	$10^{-6}$	18	65	-128.545 426	-12.105 057		
30s/15p	$10^{-4}$	11	70	-128.545 423	-12.105 033	-128.547 096	-12.108 355
30s/15p	$10^{-5}$	15	70	-128.545 426	-12.105 037		
30s/15p	$10^{-6}$	18	70	-128.545 430	-12.105 045		
32s/16p	$10^{-4}$	11	75	-128.545 410	-12.104 995	-128.547 097	-12.108 353
32s/16p	$10^{-5}$	16	75	-128.545 416	-12.105 014		
32s/16p	$10^{-6}$	19	75	-128.545 416	-12.105 013		

<sup>a</sup>Numerical values:  $E^{\text{OEPx}} = -128.5454$  a.u. (Ref. 23);  $E_x^{\text{OEPx}} = -12.1050$  a.u. (Ref. 7).

results are so small that they do not show up in the tables presented in the following.

The formalism described in the previous section has been implemented in the MOLPRO program package<sup>36</sup> for the exchange-only case. The influence of the basis set can be studied most systematically for simple atoms such as neon and argon, for which exact numerical OEP solutions are available.<sup>6,25,37</sup> In general, the Schmidt-Ruedenberg basis sets<sup>38</sup> are employed in the calculations because they can be increased in a systematic fashion, thus gradually approaching the HF basis set limit.

The OEPx results for Ne using the Schmidt-Ruedenberg<sup>38</sup> and the aug-cc-pV6Z (Ref. 39) basis sets are given in Tables I and II. Rapid convergence of the total OEPx energy toward the correct numerical value is observed for the Schmidt-Ruedenberg basis as the number of primitive Gaussian-type functions is increased. The same holds for the exchange energy also shown in Table I. It can also be seen that the threshold  $\lambda_{\min}$  for zero eigenvalues of the metric can be varied over a wide range without significantly influencing the results. The number of eigenfunctions corresponding to nonzero eigenvalues depends on this value. Remember that only these functions are needed for the expansion of the response function and the potential. Table I reveals that their number  $N_v$  is much smaller than the num-

ber of orbital products  $\psi_i\psi_a$  denoted as  $N_p$ . Thus, a large majority of the eigenvalues can be considered as zero. Note that the number of orbital products shown in Table I includes only those transforming as the completely symmetric irreducible representation of the rotation group, i.e., those with *s* character. Since the threshold  $\lambda_{\min}$  can be chosen as large as  $10^{-4}$  without deterioration of the results, it turns out that 11 functions are sufficient for a reasonably accurate representation of the response function in the case of Ne (see Table I). If the OEP results are converged, this number remains constant, i.e., independent of the size of the AO basis set.

It is illustrative to compare the results for the contracted and uncontracted aug-cc-pV6Z basis sets which are also given in Tables I and II. The decontraction has almost no effect on the HF results but leads to a considerable change of the OEP results. Note that the OEPx energy for the contracted basis set is closer to the HF energy than to the exact value. This is simply a consequence of the fact that there are now too few virtual orbitals for an accurate representation of the response function. If the number of virtual orbitals were so small that the product basis  $\psi_i\psi_a$  would become linearly independent, the HF energy would even be reproduced exactly.<sup>24</sup> The decontraction leads to a great improvement of the OEPx energy, bringing it quite close to the exact value.

TABLE II. OEPx orbital energies for Ne. The differences  $\Delta\epsilon$  between the orbital energies obtained for different AO basis sets and the ones obtained from numerical calculations ( $\epsilon_{1s}=-30.820$  a.u.,  $\epsilon_{2s}=-1.718$  a.u.,  $\epsilon_{2p}=-0.851$  a.u.) (Ref. 23) are presented. The difference  $\Delta\bar{\epsilon}_{\text{HOMO}}$  between the energy of the HOMO and the corresponding HF expectation value is also shown. All energies are given in atomic units.

Basis	$\lambda_{\min}$	$\Delta\epsilon_{1s}$	$\Delta\epsilon_{2s}$	$\Delta\epsilon_{2p}$	$\Delta\bar{\epsilon}_{\text{HOMO}}$
<i>av6z</i>	$10^{-5}$	-0.082	-0.033	-0.026	-0.026
<i>av6z</i>	$10^{-6}$	0.115	0.319	0.330	0.329
<i>av6zu</i>	$10^{-5}$	0.026	0.028	0.028	0.028
<i>av6zu</i>	$10^{-6}$	0.025	0.027	0.028	0.028
<i>16s/8p</i>	$10^{-5}$	-0.044	-0.064	-0.062	-0.063
<i>16s/8p</i>	$10^{-6}$	-0.282	-0.304	-0.303	-0.303
<i>18s/9p</i>	$10^{-5}$	-0.032	-0.020	-0.019	-0.019
<i>18s/9p</i>	$10^{-6}$	-0.034	-0.022	-0.021	-0.021
<i>20s/10p</i>	$10^{-5}$	0.048	0.045	0.045	0.045
<i>20s/10p</i>	$10^{-6}$	0.053	0.050	0.050	0.050
<i>22s/11p</i>	$10^{-5}$	0.045	0.043	0.044	0.044
<i>22s/11p</i>	$10^{-6}$	0.048	0.045	0.046	0.046
<i>24s/12p</i>	$10^{-5}$	0.007	0.009	0.010	0.010
<i>24s/12p</i>	$10^{-6}$	0.006	0.009	0.009	0.009
<i>26s/13p</i>	$10^{-5}$	-0.002	-0.003	-0.003	-0.003
<i>26s/13p</i>	$10^{-6}$	-0.004	-0.005	-0.004	-0.004
<i>28s/14p</i>	$10^{-4}$	0.018	0.016	0.016	0.016
<i>28s/14p</i>	$10^{-5}$	0.004	0.003	0.003	0.003
<i>28s/14p</i>	$10^{-6}$	0.009	0.007	0.008	0.008
<i>30s/15p</i>	$10^{-4}$	0.017	0.017	0.017	0.017
<i>30s/15p</i>	$10^{-5}$	-0.006	-0.006	-0.006	-0.006
<i>30s/15p</i>	$10^{-6}$	0.016	0.017	0.017	0.017
<i>32s/16p</i>	$10^{-4}$	0.016	0.017	0.017	0.017
<i>32s/16p</i>	$10^{-5}$	0.002	0.003	0.003	0.003
<i>32s/16p</i>	$10^{-6}$	0.010	0.011	0.011	0.011

This result clearly indicates the crucial role of the virtual orbitals for the OEP in contrast to the HF solution.

The convergence of the orbital energies is less obvious. From the differences to the correct numerical orbital energies shown in Table I, however, it can be seen that the deviations converge to a constant shift of the complete energy spectrum. Note that the energy  $\epsilon_{\text{HOMO}}$  as obtained from the one-electron Schrödinger equation [Eq. (1)] for the HOMO  $\psi_{\text{HOMO}}$  should be identical to the expectation value  $\langle\psi_{\text{HOMO}}|\hat{F}^{\text{HF}}|\psi_{\text{HOMO}}\rangle$  obtained with the HF operator  $\hat{F}^{\text{HF}}$ .<sup>25,40,41</sup> Since the HF exchange potential depends only indirectly on the local exchange potential via the occupied orbitals forming its integral kernel,  $\langle\psi_{\text{HOMO}}|\hat{F}^{\text{HF}}|\psi_{\text{HOMO}}\rangle$  is much more stable against numerical error than  $\epsilon_{\text{HOMO}}$ .<sup>7,40</sup> The values of  $\Delta\bar{\epsilon}_{\text{HOMO}}=\epsilon_{\text{HOMO}}-\langle\psi_{\text{HOMO}}|\hat{F}^{\text{HF}}|\psi_{\text{HOMO}}\rangle$  are also shown in Table II. Their agreement with the difference between the calculated and the exact orbital energies is excellent. The correct orbital energies can therefore be approached by applying a constant shift  $\langle\psi_{\text{HOMO}}|\hat{F}^{\text{HF}}|\psi_{\text{HOMO}}\rangle-\epsilon_{\text{HOMO}}$  to the calculated orbital energies. The shifted MO energies converge rapidly to their reference values. Note that constant shifts of the MO energy spectrum are also observed in numerical OEP calculations.<sup>37</sup>

The crucial role of the response function in the OEP formalism gives rise to the question if it can be properly represented in a finite orbital basis. It is therefore of interest

TABLE III. Nonzero eigenvalues of the metric in decreasing order as obtained from the Schmidt-Ruedenberg (32s/16p), the uncontracted (*av6zu*), and the contracted (*av6z*) aug-cc-pV6Z basis sets. The cutoff limit for zero eigenvalues has been set to  $10^{-5}$  in all cases.

32s/16p	<i>av6zu</i>	<i>av6z</i>
$3.733 \times 10^{-1}$	$3.733 \times 10^{-1}$	$3.730 \times 10^{-1}$
$4.215 \times 10^{-2}$	$4.216 \times 10^{-2}$	$4.200 \times 10^{-2}$
$2.066 \times 10^{-2}$	$2.065 \times 10^{-2}$	$2.013 \times 10^{-2}$
$1.183 \times 10^{-2}$	$1.178 \times 10^{-2}$	$1.151 \times 10^{-2}$
$4.704 \times 10^{-3}$	$4.683 \times 10^{-3}$	$4.447 \times 10^{-3}$
$2.526 \times 10^{-3}$	$2.407 \times 10^{-3}$	$1.811 \times 10^{-3}$
$1.599 \times 10^{-3}$	$1.387 \times 10^{-3}$	$9.950 \times 10^{-4}$
$8.946 \times 10^{-4}$	$8.333 \times 10^{-4}$	$1.583 \times 10^{-4}$
$4.419 \times 10^{-4}$	$3.369 \times 10^{-4}$	$6.459 \times 10^{-5}$
$3.164 \times 10^{-4}$	$1.411 \times 10^{-4}$	...
$1.840 \times 10^{-4}$	$7.981 \times 10^{-5}$	...
$8.864 \times 10^{-5}$	$5.892 \times 10^{-5}$	...
$4.974 \times 10^{-5}$	$2.274 \times 10^{-5}$	...
$2.871 \times 10^{-5}$	$1.375 \times 10^{-5}$	...
$1.429 \times 10^{-5}$	...	...
$1.184 \times 10^{-5}$	...	...

to examine the dependence of its eigenvalues on the size of the AO basis set. The nonzero eigenvalues of the metric as defined by Eq. (38) are given in Table III for three different basis sets: the Schmidt-Ruedenberg (32s/16p) basis set and the aug-cc-pV6Z basis set both contracted and uncontracted. The eigenvalues of the response function are obtained by multiplication with  $-2$  [see Eq. (41)]. A clear trend toward a converging eigenvalue spectrum is observed although the (32s/16p) Schmidt-Ruedenberg and the aug-cc-pV6Z basis sets yield different orbital energy spectra for the virtual orbitals (not shown) in the case of both HF and OEPx. The convergence of the eigenvalues is much faster in the upper part of the spectrum, where already the eigenvalues obtained with the contracted aug-cc-pV6Z basis set are close to those obtained for the larger basis sets. The convergence of the eigenvalues indicates that a point can be reached where an increase of the orbital basis mainly leads to additional eigenfunctions with small eigenvalues without changing the relevant part of the spectrum. For sufficiently large basis sets, most of these eigenfunctions will be eliminated by employing a threshold for near-zero eigenvalues. Table I shows that the nonvanishing eigenvalues represent only a small minority of the complete spectrum for the larger AO basis sets.

The results of the OEPx calculations for Ar are shown in Tables IV and V. The same general trends as for Ne are observed although the convergence to the numerical OEPx results is somewhat slower so that larger basis sets are needed as compared to the case of Ne. Nonetheless, the number of 16 functions needed for a good representation of the response function is still fairly small.

## IV. CONCLUSION

Coming back to the question in the title of this paper, we conclude that a convergence of the eigenvalue spectrum of the response function is indeed observed if the size of the orbital basis set is increased. At the same time, the OEP



TABLE IV. OEPx results for Ar using uncontracted Schmidt-Ruedenberg basis sets of various sizes and the aug-cc-pV6Z basis sets both contracted (*av6z*) and uncontracted (*av6zu*). The first column shows the number of primitive Gaussian-type functions for the *s* and *p* atomic orbitals in the case of the Schmidt-Ruedenberg basis. The threshold for zero eigenvalues of the metric is given in the second column.  $N_v$  is the number of eigenfunctions with nonzero eigenvalues.  $N_p$  is the number of orbital products.  $E^{\text{OEPx}}$  and  $E_x^{\text{OEPx}}$  are the total electronic and the exchange energies, respectively, as obtained from the OEPx calculations. The corresponding HF values are denoted as  $E^{\text{HF}}$  and  $E_x^{\text{HF}}$ . All energies are given in atomic units.

Basis	$\lambda_{\min}$	$N_v$	$N_p$	$E^{\text{OEPx}}$ <sup>a</sup>	$E_x^{\text{OEPx}}$ <sup>a</sup>	$E^{\text{HF}}$	$E_x^{\text{HF}}$
<i>av6z</i>	$10^{-5}$	11	30	-526.816 023	-30.182 440	-526.817 484	-30.184 935
<i>av6z</i>	$10^{-6}$	12	30	-526.816 048	-30.182 412		
<i>av6zu</i>	$10^{-5}$	17	83	-526.812 554	-30.175 309	-526.817 484	-30.184 934
<i>av6zu</i>	$10^{-6}$	21	83	-526.812 600	-30.175 385		
20s/13p	$10^{-5}$	15	73	-526.812 222	-30.176 313	-526.816 966	-30.185 195
20s/13p	$10^{-6}$	18	73	-526.812 224	-30.176 321		
22s/14p	$10^{-5}$	16	81	-526.812 789	-30.176 479	-526.817 292	-30.185 059
22s/14p	$10^{-6}$	19	81	-526.812 807	-30.176 572		
24s/15p	$10^{-5}$	17	89	-526.812 591	-30.175 532	-526.817 417	-30.184 995
24s/15p	$10^{-6}$	20	89	-526.812 654	-30.175 691		
26s/16p	$10^{-5}$	17	97	-526.812 387	-30.175 172	-526.817 467	-30.184 969
26s/16p	$10^{-6}$	21	97	-526.812 409	-30.175 188		
28s/17p	$10^{-5}$	17	105	-526.812 484	-30.175 394	-526.817 491	-30.184 957
28s/17p	$10^{-6}$	21	105	-526.812 520	-30.175 506		
30s/18p	$10^{-5}$	18	113	-526.812 507	-30.175 302	-526.817 503	-30.184 950
30s/18p	$10^{-6}$	21	113	-526.812 516	-30.175 333		
32s/19p	$10^{-4}$	15	121	-526.812 334	-30.174 857	-526.817 508	-30.184 946
32s/19p	$10^{-5}$	18	121	-526.812 389	-30.174 991		
32s/19p	$10^{-6}$	22	121	-526.812 431	-30.175 074		
50s/28p	$10^{-4}$	16	193	-526.812 221	-30.174 669	-526.817 513	-30.184 942
50s/28p	$10^{-5}$	22	193	-526.812 239	-30.174 710		
50s/28p	$10^{-6}$	27	193	-526.812 239	-30.174 708		
52s/29p	$10^{-4}$	16	201	-526.812 194	-30.174 604	-526.817 513	-30.184 942
52s/29p	$10^{-5}$	22	201	-526.812 246	-30.174 770		
52s/29p	$10^{-6}$	27	201	-526.812 250	-30.174 787		

<sup>a</sup>numerical values:  $E^{\text{OEPx}} = -526.8122$  a.u. (Ref. 23);  $E_x^{\text{OEPx}} = -30.1748$  a.u. (Ref. 7).

energy approaches the correct value as obtained numerically for the noble gas atoms Ne and Ar. Rather limited numbers of 11 and 16 eigenfunctions for Ne and Ar, respectively, proven to be sufficient for a reasonably accurate representation of the response function. It is an important result of the present investigation that the number of relevant eigenfunctions of the response function is relatively small and independent of the size of the AO basis set provided that the latter is not too small. The convergence of the response function is not surprising if one takes into account that the asymptotic behavior of the orbital products  $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$  is determined by the occupied orbitals which decay rapidly, thus being nonzero only in a rather limited region of space. The orbital products are confined to the same region. The limited spatial extension of that region makes it possible to expand any sufficiently smooth function within that region by a limited number of basis functions. Since the eigenfunctions of the response function must be orthogonal and the virtual orbitals become more rapidly oscillating as the orbital energy increases, one must reach a point where the addition of more orbital products only produces more rapidly oscillating eigenfunctions of the response function. However, these eigenfunctions correspond to very small eigenvalues thus being removed from the representation of the response function

by employing a cutoff parameter for near-zero eigenvalues. It is just this behavior that has been observed in our numerical calculations.

It is important to note that rather large basis sets are needed to get close to the correct OEP solution for Ne and Ar. The fact that a certain contracted basis set closely approaches the HF limit is meaningless with respect to OEPx. This has been demonstrated for the contracted aug-cc-pV6Z basis set for Ne and Ar, where the decontraction of the basis set has no visible effect on the HF energies but greatly improves the OEPx energies. In contrast to the HF limit which is always approached from above, there is no such regularity for the convergence to the correct OEPx energy as can be seen from the OEPx energy obtained with the contracted aug-cc-pV6Z basis set, which is lower than the numeric OEPx energy. This also resolves the seemingly paradoxical observation of Staroverov *et al.*<sup>24</sup> that there is an infinite number of local potentials reproducing the HF energy: the AO basis sets used by these authors are simply too small. Basis sets large enough for an appropriate solution of the OEP necessarily result in a linear dependence of the orbital products  $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$ . In this case, the relationship  $v_{ia}^x = v_{ia}^{x,\text{nl}}$  used as a starting point by Staroverov *et al.*<sup>24</sup> breaks down.<sup>11</sup> This follows from Eq. (37) which has been used by Staroverov *et al.*<sup>24</sup> for the determination of the local ex-

TABLE V. OEPx orbital energies for Ar. The differences  $\Delta\epsilon$  between the orbital energies obtained for different AO basis sets and the ones obtained from numerical calculations ( $\epsilon_{1s}=-114.452$  a.u.,  $\epsilon_{2s}=-11.153$  a.u.,  $\epsilon_{3s}=-1.099$  a.u.,  $\epsilon_{2p}=-8.734$  a.u.,  $\epsilon_{3p}=-0.591$  a.u.) (Ref. 23) are presented. The difference  $\Delta\bar{\epsilon}_{\text{HOMO}}$  between the energy of the HOMO and the corresponding HF expectation value is also shown. All energies are given in atomic units.

Basis	$\lambda_{\min}$	$\Delta\epsilon_{1s}$	$\Delta\epsilon_{2s}$	$\Delta\epsilon_{3s}$	$\Delta\epsilon_{2p}$	$\Delta\epsilon_{3p}$	$\Delta\bar{\epsilon}_{\text{HOMO}}$
av6z	$10^{-5}$	-0.649	-0.089	-0.027	-0.051	-0.022	-0.022
av6z	$10^{-6}$	-0.662	-0.170	-0.098	-0.131	-0.094	-0.094
av6zu	$10^{-5}$	-0.025	-0.019	-0.014	-0.018	-0.014	-0.014
av6zu	$10^{-6}$	0.118	0.124	0.131	0.126	0.132	0.132
20s/13p	$10^{-5}$	0.092	0.100	0.082	0.101	0.083	0.083
20s/13p	$10^{-6}$	0.087	0.095	0.077	0.096	0.078	0.078
22s/14p	$10^{-5}$	0.085	0.091	0.084	0.092	0.085	0.085
22s/14p	$10^{-6}$	-0.040	-0.037	-0.045	-0.036	-0.044	-0.044
24s/15p	$10^{-5}$	0.022	0.025	0.034	0.026	0.034	0.034
24s/15p	$10^{-6}$	-0.217	-0.215	-0.204	-0.214	-0.204	-0.204
26s/16p	$10^{-5}$	-0.020	-0.018	-0.018	-0.017	-0.018	-0.018
26s/16p	$10^{-6}$	-0.127	-0.127	-0.125	-0.126	-0.125	-0.125
28s/17p	$10^{-5}$	-0.025	-0.024	-0.030	-0.024	-0.029	-0.029
28s/17p	$10^{-6}$	0.119	0.121	0.114	0.121	0.114	0.114
30s/18p	$10^{-5}$	-0.015	-0.012	-0.012	-0.011	-0.012	-0.012
30s/18p	$10^{-6}$	0.003	0.004	0.003	0.005	0.004	0.004
32s/19p	$10^{-4}$	-0.022	-0.020	-0.017	-0.020	-0.017	-0.017
32s/19p	$10^{-5}$	0.014	0.015	0.018	0.015	0.018	0.018
32s/19p	$10^{-6}$	0.049	0.048	0.052	0.049	0.052	0.052
50s/28p	$10^{-4}$	0.023	0.023	0.023	0.023	0.023	0.023
50s/28p	$10^{-5}$	0.005	0.005	0.006	0.005	0.006	0.006
50s/28p	$10^{-6}$	0.012	0.012	0.013	0.012	0.013	0.013
52s/29p	$10^{-4}$	0.025	0.026	0.027	0.026	0.027	0.027
52s/29p	$10^{-5}$	0.025	0.025	0.024	0.025	0.024	0.024
52s/29p	$10^{-6}$	-0.001	-0.001	-0.002	-0.001	-0.002	-0.002

change potential: the latter equation can only be solved if the matrix representing the metric of the orbital products  $\psi_a(\mathbf{r})\psi_i(\mathbf{r})$  is nonsingular. We refer once more to the difference between Eqs. (31) and (32) where only the former corresponds to an appropriate matrix representation of the OEP equation [Eq. (6)].

The seemingly high requirements with respect to the AO basis sets used for the solution of the OEP integral equation raise some questions about the general applicability of this method to larger molecules. It is obvious from the preceding considerations that the contracted Gaussian basis sets commonly used in quantum chemical calculations are not appropriate for the solution of the OEP problem. Since the response function is such a crucial ingredient in the OEP formalism, the design of basis sets enabling its sufficiently accurate representation is highly desirable. The Schmidt-Ruedenberg basis sets<sup>38</sup> used in our investigation have been developed for systematically approaching the HF limit for smaller atoms but not with respect to a good representation of the response function. Having the latter in mind, it is important to find a reasonable compromise between the size of the basis set and the accuracy of the response function. The method employed in this investigation might provide an important analytical tool with respect to this task. Note that the problems with the choice of an appropriate AO basis set are avoided in approximations to OEPx such as KLI (Refs. 25 and 26) or the local Hartree-Fock method<sup>27</sup> with the latter

being equivalent to CEDA.<sup>16</sup> These approximations circumvent the difficulties arising from the virtual orbitals by using the completeness of the MO basis to eliminate them completely.

Although the present method is the only one offering a possibility to study the properties of the response function for finite orbital basis sets in a systematic way its usefulness with respect to practical OEP calculations is limited. Note that the number of orbital products increases as  $N^2$  if  $N$  is the number of AO basis functions. Thus, matrix operations involving the metric  $\mathbf{M}$  defined in Eq. (14) scale as  $N^6$ . This unfavorable scaling behavior is prohibitive with respect to practical applications. The expansion of the local potential in an auxiliary basis which is already common practice<sup>10,12,14,15,17,20</sup> can therefore not be avoided. It is of particular importance that the number of auxiliary functions grows only linearly with the system size. An empirical scheme for balancing auxiliary and AO basis sets has been presented very recently and has been applied with great success to atoms and molecules.<sup>12</sup> It might be of interest to study the relationship between the auxiliary basis and the eigenfunctions of the response function. Intuitively, one would expect that the auxiliary functions should span approximately the same space as these eigenfunctions. In this case the present method could also be useful for the design of auxiliary basis sets. It can be expected that the number of relevant eigenfunctions of the response function grows as the spatial region where these functions are nonvanishing which is determined by the spatial extension of the occupied orbitals. This would correspond to a linear increase with the system size in contrast to the quadratic increase of the number of orbital products.

The OEP method is still far from the stage of practical applicability to real chemical problems. Some fundamental questions remain to be resolved which are partly of a purely mathematical character. The present work was intended to address one of these basic problems, i.e., the choice of appropriate AO basis sets for OEP calculations. Questions of this kind have to be resolved before the method can prove its practical usefulness.

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